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SELECTIVE STRONTIUM REMOVAL FROM A SODIUM NITRATE AQUEOUS MEDIUM BY NANOFILTRATION - COMPLEXATION

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ABSTRACT

In aqueous medium, selective complexation increases the ionic separation by nanofiltration. The combination of nanofiltration and complexation can be applied to the nuclear effluents treatment. To separate radioelements from a sodium salt medium, poly(acrylic acid) is associated to the FILMTEC NF 70 membrane. Effects of transmembrane pressure, pH, ligand concentration and ionic strength on salts retention are described, and the complexation constants are estimated. Finally, to reach the objectives, a strontium two - stages concentration by nanofiltration - complexation with a control of retentate salinity is investigated in a nonactive solution case.

INTRODUCTION

Nanofiltration is a pressure - driven membrane process with membrane pore sizes between those of ultrafiltration and reverse osmosis. The nanofiltration membrane "cut -

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off" lies in the molecular weight range of 300 - 1000 kg / kmol (1, 2). Organic, mineral or composite nanofiltration membranes have pores which can be electrically charged and have been widely studied during this last decade for separation of ionic species (1 - 4).

Water (5) and milk treatment, paper mill waste treatment (6), and pharmaceutical separations are some applications for this kind of membrane (7). This is one of the cheapest processes to produce drinking water from brine water (3, 8) because transmembrane pressures of nanofiltration are lower than those of reverse osmosis. For example, the FILMTEC NF 70 membrane is used to decontaminate solutions containing pesticides of molecular weights around 250 kg/kmol. Molecular weight and electrostatic or chemical interaction between pesticides and the membrane are responsible for the organic solutes retention (9).

Nuclear effluents usually contain traces of radioelements in a sodium salt medium. Radioelements can be stored in a vitreous matrix, but the high sodium salt excess is undesirable for vitrification. Thus, sodium salt / radioelements separation is necessary. This separation can be carried out by precipitation or by solid-liquid or liquid-liquid extraction, but these processes produce other wastes such as elution or stripping reagents, whereas nanofiltration process produces hardly any additional waste. However, ionic separation using nanofiltration is sometimes insufficient, such as in the case of nuclear effluents decontamination. Association of a filtration system with a complexation step increases selectively the retention of a target element (ion) : in the nanofiltration case, ligands must be water soluble and larger than the membrane "cut - off". In this way, the target element retention is improved because those ions become complexed by the ligand and don't pass through the membrane. Studies of combined filtration (microfiltration, ultrafiltration, nanofiltration, reverse osmosis) and complexation have been made with poly(acrylic acid) (10 - 16), polyethylenimin (13 - 17) and EDTA (16, 18, 19). The use of nanofiltration in such a combination will broaden the range of complexants that can be used : ligands with low molecular weight (about 500 kg / kmol) can be studied and viscosity problems encountered in microfiltration or in ultrafiltration are reduced.

Objective.

Nuclear effluents usually contain traces of radioelements in a sodium salt solution. For nanofiltration to be effective for this problem, it must produce :

1) A small volume of retentate that contains the ligand and at least 99 % of the radioelements initially present in the model solution.

2) A permeate fraction containing 90 % of the sodium salt initially present and radioelements at concentration equal or below those permitted for discharge of the waste.

Experimental

The experimental nanofiltration loop is presented in the figure 1. By recycling totally the permeate (a), the feed remains at constant composition during the nanofiltration. On the other hand, by extracting the permeate (b), the feed can be concentrated. To keep a constant salinity in the retentate, water (c) can be added during a concentration step. Finally to simulate a multi - stage nanofiltration, a pump (d) transfers the extracted permeate (b) in the feed tank to be used to test the next stage.

The model solutions used in these studies have to represent the nuclear effluent. They contain strontium and cesium at trace concentrations that can be determined by atomic absorption spectrometry (mmol / L), in a sodium salt medium (mol / L). These non-radioactive solutions are prepared by dissolution in distilled water of the appropriate salts and ligand :

-Sodium nitrate 99 % (Prolabo)
-Strontium nitrate 99 % (Aldrich)
-Cesium nitrate 99 % (Aldrich)
-Poly(acrylic acide), 2000 kg / kmol, 65 wt. % solution in water (Aldrich)

Retentions (Ri), transmission coefficients (Ti), decontamination factors (DFi), volumetric concentration factors (VCF) and dilution factors (df) are calculated as follows.

$$Ri = ((Mir - Mip) / Mir) . 100$$

$$Ti = 100 - Ri$$

$$DFi = Mir / Mip$$

$$VCF = Vor / Vr$$

$$df = VT / Vor$$

Mir = Initial i solute mass in the retentate.
Mip = i solute mass in the permeate.
Vor = Initial retentate volume.
Vr = Retentate volume.
VT = Total permeate and retentate volume.

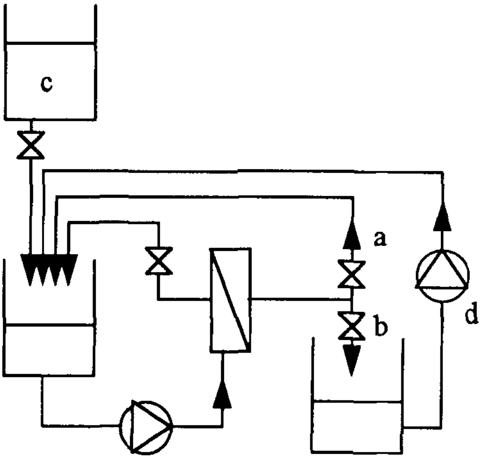

FIGURE 1. Nanofiltration apparatus scheme.

N.B. : To calculate retention (Ri) and decontamination factor (DFi) when permeate is recycled, Mip and Mir are respectively replaced by Cip and Cir (i solute concentration in the permeate and in the retentate) because the feed volume is constant.

RESULTS AND DISCUSSION

Transmembrane Pressure Effect on Salts Retention without Ligand

Nanofiltration was carried out with the FILMTEC NF 70 membrane. The model solution contained traces of cesium and strontium in a sodium nitrate excess. The transmembrane pressure effect on salts retention and filtration fluxes is presented in figure 2. For all transmembrane pressures, cesium shows the lowest retention while strontium presents the highest retention. Size, charge and mobility of ions are the main parameters which can be involved in the salt transmembrane transfer (20). Mobility effects on salts retention by a charged membrane have been shown with dilute solutions in the case of counter-ions mixtures (21, 22). Surface charges on FILMTEC NF 70 membrane are assumed to be negative (4, 7, 20), and nitrate ions are the only membrane

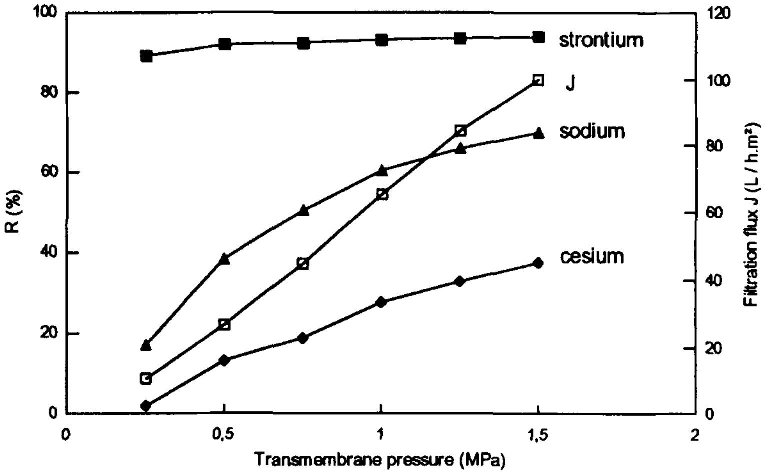

FIGURE 2. Transmembrane pressure effect on ionic retentions and filtration fluxes. $[Na^+] = 90$ mmol/L, $[Sr^{2+}] = 0.28$ mmol/L, $[Cs^+] = 0.19$ mmol/L, pH = 4.5, T = 300 K.

co-ions. Moreover, the excess of sodium screens the negative surface charges of the membrane, so ionic separation by co-ion exclusion is reduced. In this case, ionic size is the main parameter controlling retention, if ions pairing is neglected. Ionic retention rises with the hydration free energy (Sr^{2+} (1447 kJ / mol), Na^+ (411 kJ / mol), Cs^+ (284 kJ / mol)) (23, 24).

On the other hand, cesium and sodium retentions increase with transmembrane pressure, while those of strontium are nearly constant. Thus, sodium salt / strontium separation is optimal at low transmembrane pressure (0.5 MPa), while sodium salt / cesium separation is poor whatever the filtration flux.

To concentrated traces of strontium or cesium in a sodium salt medium, the performance of FILMTEC NF 70 membrane is inadequate. To increase membrane selectivity, the combination of nanofiltration and complexation was investigated. Both strontium and cesium complexations are studied using the poly(acrylic acid) ligand.

Poly(acrylic acid) - FILMTEC NF 70 Association for the Sodium Salt / Radioelement Separation

pH effect on salts retention. Model solution contains poly(acrylic acid), cesium and strontium traces in a sodium salt medium and nanofiltration were used along with the

FILMTEC NF 70 membrane. The effect of pH on salts retention and filtration fluxes is presented in the figure 3. Above pH 6, carboxilic acid deprotonation (pKa = 4 - 5 (25)) allows strontium to become complexed ; consequently, strontium retention increases sharply. In these experimental conditions, strontium hydroxide concentrations are not important.

Both cesium and sodium retentions increase with pH, but no complexation reaction is involved, and the same variation is noticed with or without ligand : a surface charge modification or a membrane swelling with pH can explain these increases in retention. However filtration fluxes are constant whatever the pH.

Poly(acrylic acid) concentration effect on salts retention. The model solution contains traces of strontium in a sodium nitrate medium. The influence of poly(acrylic acid) concentration on salts retention and filtration fluxes is presented in figure 4. Strontium retention increases with poly(acrylic acid) concentration, while the ligand concentration has no significant effect on sodium retention. In this way, sodium salt / strontium separation is improved. But a large excess of ligand is necessary ([-COOH] / [Sr^{2+}] = 100) to reach a strontium retention of 98.6 %. To evaluate the complexation constants ($\beta(ML_n)$), some assumptions have been made by taking experimental conditions into account :

-Strontium hydroxides amounts are neglected,

-Poly(acrylic acid) is totally rejected,

-Carboxilic acids are only in ionic form or in metal complex form :

$$2(\text{-COO}^-) + Sr^{2+} \Leftrightarrow (\text{-COO}_2Sr) \qquad \beta(\text{-COO}_2Sr)$$
$$(\text{-COO}^-) + Na^+ \Leftrightarrow (\text{-COONa}) \qquad \beta(\text{-COONa})$$

The complexation constants, $\beta(ML_n)$, are given by Eq. **I** :

$$\boxed{\beta(ML_n) = \frac{[ML_n]}{[M].[L]^n}} \qquad \text{I}$$

The concentration of uncomplexed cation, [M], is expressed by Eq. **II** :

$$[M] = [M_T].\frac{T^i_{(M)}}{T^0_{(M)}} \qquad \text{II}$$

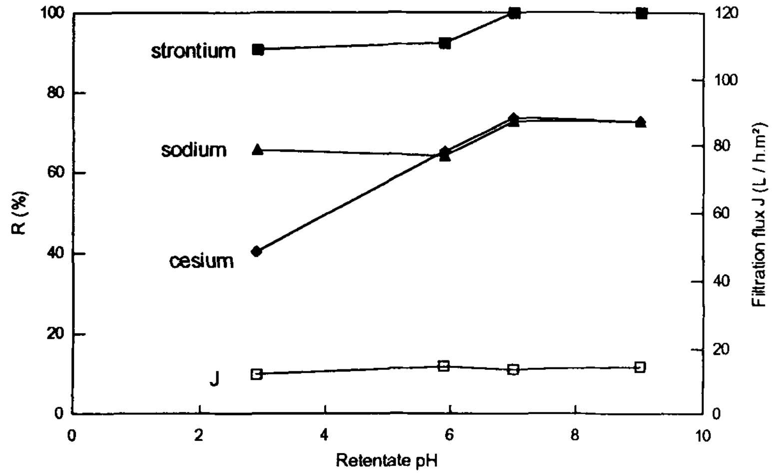

FIGURE 3. Retentate pH effect on ionic retentions and filtration fluxes. $[Na^+] = 90$ mmol/L, $[Sr^{2+}] = 0.28$ mmol/L, $[Cs^+] = 0.19$ mmol/L, $[\text{-COOH}] / ([Sr^{2+}] + [Cs^+]) = 2$, $\Delta P = 0.5$ MPa, T = 298 K.

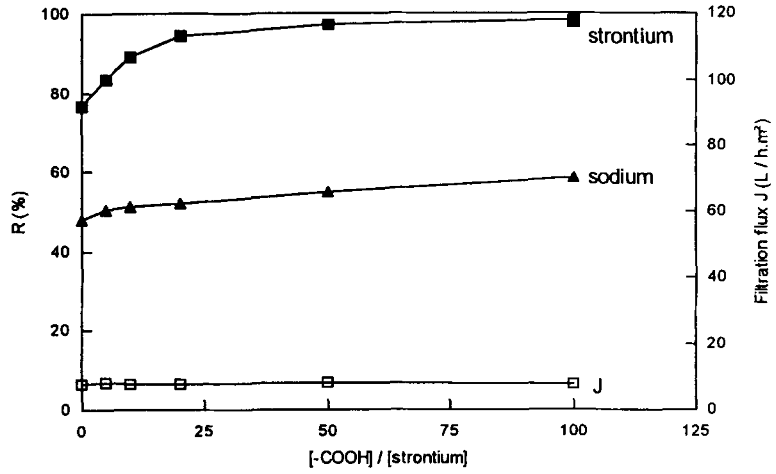

FIGURE 4. Poly(acrylic acid) concentration effect on ionic retentions and filtration fluxes. $[Na^+] = 150$ mmol/L, $[Sr^{2+}] = 0.28$ mmol/L, $\Delta P = 0.5$ MPa, pH = 9, T = 298 K.

where $[M_T]$ is the total cation concentration, $T^i_{(M)}$ is the transmission coefficient for cation with ligand and $T^0_{(M)}$ is the transmission coefficient for cation without ligand. Using the Eq. **II**, the complex concentration, $[ML_n]$, is calculated (Eq. **III**) :

$$[ML_n] = [M_T] - [M] \Leftrightarrow [ML_n] = [M_T].(1 - \frac{T^i_{(M)}}{T^0_{(M)}}) \qquad \text{III}$$

The free ligand concentration, [L], is given by Eq. **IV** :

$$[L] = [L_T] - n.[ML_n] \Leftrightarrow [L] = [L_T] - n.[M_T].(1 - \frac{T^i_{(M)}}{T^0_{(M)}}) \qquad \text{IV}$$

From Eqs. **I**, **II**, **III** and **IV**, complexation constants ($\beta(ML_n)$) are easily calculated (Eq. **V**) :

$$\boxed{\beta(ML_n) = \frac{1 - y}{y.[L_T]^n.(1 - nx(1 - y))^n}} \qquad \text{V}$$

$$\text{with} \quad x = \frac{[M_T]}{[L_T]} \quad \text{and} \quad y = \frac{T^i_{(M)}}{T^0_{(M)}}$$

At first, strontium complexation constants weaken when the ionic strength is increased (Table 1). Secondly, from the salts retentions results, it is clear that the strontium complexation constants are larger than the sodium constants. However, the gap between the two complexation constants is insufficient to separate strontium from a sodium salt medium if poly(acrylic acid) concentration isn't present in excess.

During the experiment no membrane fouling was observed, and filtration fluxes were constant. Irreversible membrane fouling was avoided because this ligand molecular weight (2000 kg / kmol) is significantly larger than the membrane "cut - off" (about 300 kg / kmol with uncharged solute). Concentration polarization is limited because transmembrane pressure and filtration fluxes are weak.

TABLE 1. SALINITY EFFECT ON COMPLEXATION CONSTANTS

$[NaNO_3]$ (mol / L)	log $\beta(-COO_2Sr)$	log $\beta(-COONa)$	Reference
0	8.5	-	26
0.1	6.8	-	26
0.15	4.3[a]	0.8[a]	Calculated (Eq. V)

[a] : $[Na^+]$ = 150 mmol/l, $[Sr^{2+}]$ = 0.26 mmol/L, [COOH] = 28.5 mmol/L, ΔP = 0.5 MPa, pH = 9, T = 298 K

Ionic strength effect on salts retention. This model solution contains strontium traces and poly(acrylic acid) in a sodium nitrate solution. The influence of sodium nitrate concentration on salts retention and filtration fluxes is shown in figure 5 : when the salinity increases, both sodium and strontium retentions decrease. Some proposed explanations are :

-The addition of sodium counter-ion screens the negative surface charges of the membrane. Consequently, nitrate co-ion can pass through the membrane without being rejected by the fixed negative charges (20, 27). To maintain electroneutrality in both permeate and retentate, nitrates migrate with their counter-ion, strontium and sodium, but in our case, charge effects on ionic exclusion are negligible.

-The degree of ionic hydration declines when the ionic strength is raised.

-Complexation equilibria are shifted to form more sodium complex.

-When ionic strength increases, poly(acrylic acid) takes a coil conformation and the number of accessible carboxilic acid decreases.

As expected, filtration fluxes decline when the salinity is raised : FILMTEC NF 70 membrane exhibits significant sodium salt retention,which generates a salinity difference between permeate and retentate. Osmotic pressure increases with this salinity difference, and the filtration fluxes then decline.

Strontium Two-Stage Concentration by Nanofiltration-Complexation. Application to the Treatment of a Model Solution which Represents a Nuclear Effluent.

A two-stage nanofiltration (cf. figure 1) is investigated to increase sodium / strontium separation. The model solution contains traces of strontium in a sodium nitrate

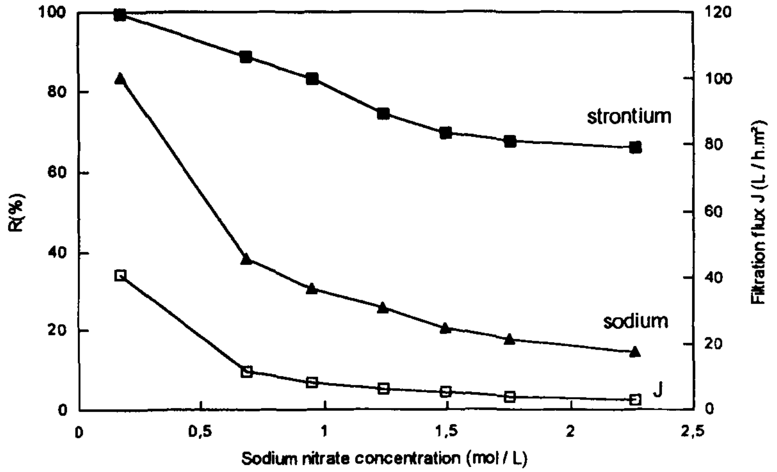

FIGURE 5. Ionic strength effect on ionic retentions and filtration fluxes. $[Sr^{2+}] = 0.28$ mmol/L, $[\text{-COOH}] / [Sr^{2+}] = 100$, $\Delta P = 1.5$ MPa, pH = 9, T = 293 K.

medium. The objectives of the two stage nanofiltration-complexation are to obtain :

-A small volume fraction including ligand and at least 99 % of radioelements initially present in the model solution.

-A large fraction containing 90 % of the sodium salt initially present in the model solution.

To reach this goal, a strontium retention of 90 % is necessary for each stage. Strontium retention is greater than 90 % if the sodium nitrate concentration is less than or equal to 0.5 mol / L (figure 5). During concentration, the salinity must be stabilized to 0.5 mol / L by diafiltration ; the retentate conductimetric measurement is unsuitable to estimate salinity by the fact that the concentration of ligand is high. Figure 5 shows that sodium retention depends on its own retentate concentration: thus, the salinity fluctuation in the retentate is estimated by permeate conductimetric measurement ; if necessary, simultaneous water additions are made to correct for these fluctuations.

In fact, a loop rinse is required between the consecutive concentrations, because the two-stage nanofiltration is carried out on the same apparatus. Rinse solution must have the same sodium salt concentration as the first extracted permeate. Such a saline

TABLE 2. RESULTS OF THE STRONTIUM TWO-STAGE CONCENTRATION BY NANOFILTRATION-COMPLEXATION WITH A RETENTATE SALINITY CONTROL BY DIAFILTRATION.

	Stage 1[a]	Stage 2[b]	Stage (1 + 2)
Filtration Fluxes Density ($L / h{\cdot}m^2$)	16	24	**20**
df (Dilution Factor)	1.9	1.25	**2.35**
R Sr^{2+}(%)	85.2	88.8	**98.2**
R Na^+ (%)	19.15	19.4	**28.2**
VCF	6.66	11.95	**3.4**

[a] : $[Na^+]$initial = 500 mmol/L, $[Sr^{2+}]$initial = 0.28 mmol/L, [-COOH] / $[Sr^{2+}]$ = 100, Vor = 30 L, ΔP = 1.5 MPa, pH = 10, T = 298 K.

[b] : $[Na^+]$initial = 240 mmol/L, $[Sr^{2+}]$initial = 0.024 mmol/L, [-COOH] / $[Sr^{2+}]$ = 350, Vor = 52.6 L, ΔP = 1.5 MPa, pH = 10, T = 298 K.

rinse allows a maximal elimination of residual strontium and fouling species from the filtration loop after the first concentration,and a membrane saline conditioning before the second concentration stage.

Results presented in Table 2 don't take in account this saline rinse. The global strontium retention is slightly lower than 99 % because water additions (df = 2.35) increase the permeate mass and consequently results in an additional strontium leakage. The permeate fraction only contains 71.8 % of the total sodium salt (against 90 % as objective) because the extracted permeate mass represents 70 % of the mass initially present in the model solution (Volumetric concentration factor = 3.4). By increasing the volumic concentration factor, the sodium salt elimination rises. The salinity of the second extracted permeate is lower than that of the first permeate because of the sodium salt retention by FILMTEC NF 70 membrane. Filtration fluxes are lower in the first stage because the osmotic pressure is stronger.

In summary, high sodium salt retention with FILMTEC NF 70 membrane involves :

-A high transmembrane pressure to avoid filtration fluxes decline (osmotic pressure)

-Water additions to keep salinity constant during concentration,

-A decline in strontium retention because of the permeate mass increase.

CONCLUSION

Selective complexation is combined with a nanofiltration membrane. In this way, the sodium salt / strontium separation of the FILMTEC NF 70 membrane is increased. Nonradioactive solutions containing traces of strontium in a sodium nitrate solution have been studied in alkaline medium. Poly(acrylic acid) is a strontium ligand,but the effects of strontium selective complexation are reduced by the excess of sodium salt. To reach the objectives of this program, a two-stage strontium concentration was investigated. During concentration, the retentate salinity is maintained constant by water additions (diafiltration). In this way, 98.2 % of strontium was concentrated (VCF = 3.4) and more than 70 % of sodium nitrate is eliminated from the retentate. Experiments using FILMTEC NF 70 membrane show that a high sodium salt retention involves a decline in filtration fluxes, large water addition to stabilize retentate salinity during concentrations, and a decrease in strontium retention. New nanofiltration membrane with low sodium salt retention should be more suitable for this separation and are actually studied. Moreover, simultaneous cesium and strontium complexation may be reach with suitable ligands.

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